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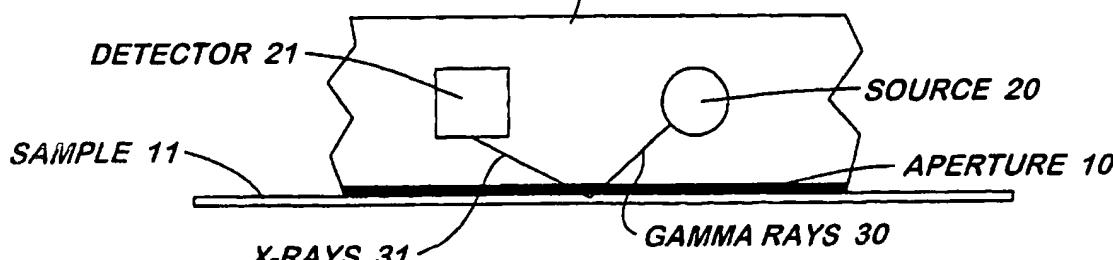
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(54) Title: METHODS FOR IDENTIFICATION AND VERIFICATION

XRF INSTRUMENT HOUSING 15



(57) Abstract: An apparatus and method in which one or more taggants that are intrinsically located or extrinsically placed in an article or product (11). The taggants are detected by X-ray fluorescence analysis (20, 21) to identify or verify the article of its point of manufacture. The taggants are manufactured as part of the article or the taggant is placed into a coating, label, or otherwise embedded within the article for the purpose of later verifying the presence or absence of these elements by X-ray fluorescence, thus determining the unique elemental composition of the taggant within the article.

WO 01/25767 A1

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## METHODS FOR IDENTIFICATION AND VERIFICATION

### REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of U.S. Provisional Application Serial No. 60/157,573, the disclosure of which is incorporated herein by reference.

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### FIELD OF THE INVENTION

The present invention generally relates to apparatus and methods for identification and verification. More particularly, the present invention relates to apparatus and methods for detecting an element or compound intrinsically present—or extrinsically added—in an article or product by using X-ray fluorescence to identify and verify that article or product.

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### BACKGROUND OF THE INVENTION

There has been significant interest in apparatus and methods for identifying and verifying various articles or products such as explosives, ammunition, paint, petroleum products, and documents. Known methods used to identify and verify generally involve adding and detecting materials like code-bearing microparticles, bulk chemical substances, and radioactive substances. Other methods used for identifying and verifying articles include those described in U.S. Patent Nos. 6,030,657, 6,024,200, 6,007,744, 6,005,915, 5,760,394, 5,474,937, 5,301,044, 5,208,630, 5,057,268, 4,862,143, 4,390,452, 4,363,965, and 4,045,676, the disclosures of which are incorporated herein by reference.

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It is also known to apply materials to articles in order to track, for example, point of origin, authenticity, and their distribution. In one method, inks which are transparent in visible light are sometimes applied to materials and the presence (or absence) of the ink is revealed by ultraviolet or infrared fluorescence. Other methods

include implanting microscopic additives which can be detected optically. However, detecting these materials is primarily based on optical or photometric measurements.

Unfortunately, many of the apparatus and methods for identifying and verifying articles using such materials (called taggants) are unsatisfactory for several 5 reasons. First, they are often difficult and time-consuming. In many instances, a sample of the article must be sent to an off-site laboratory for analysis. In other instances, the apparatus are often expensive, large, and difficult to operate. In yet other instances, the taggant used is radioactive, causing serious health concerns.

The known apparatus and methods for identification and verification are also 10 unsatisfactory because they require a "line-of-sight" analysis method. This line of sight requirement entails that the apparatus must be able to "see" the taggant in order to detect it. This can be detracting when it would be desirable to detect the taggant without having to see the taggant, e.g., such as when the taggant is located in the middle of large package with packaging and labels "covering" the taggant.

15 SUMMARY OF THE INVENTION

The present invention provides an apparatus and method in which one or more taggants that are intrinsically located—or extrinsically placed—in an article or product are detected by x-ray fluorescence analysis to identify or verify the article or 20 its point of manufacture. The taggants are manufactured as part of the article or the taggant is placed into a coating, packaging, label, or otherwise embedded within the article for the purpose of later verifying the presence or absence of these elements by x-ray fluorescence to determine the unique elemental composition of the taggant within these articles.

By using x-ray fluorescence analysis, the apparatus and methods of the present 25 invention are simple and easy to use, as well as provide detection by a non line-of-sight method to establish the origin of materials, point of manufacture, authenticity, verification, or product security. The present invention is extremely advantageous because it is difficult to replicate, simulate, alter, transpose, or tamper. Further, it is easily recognizable by a user in either overt or covert form, verifiable by a

manufacturer or issuer, and is easily applicable to various forms of media in the articles.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1, 2a, 2b, 3, 4a, 4b, and 5-7 are views of apparatus and methods for 5 identification and verification according to the present invention. Figures 1, 2a, 2b, 3, 4a, 4b, and 5-7 presented in conjunction with this description are views of only particular—rather than complete—portions of apparatus and methods for identification and verification.

#### DETAILED DESCRIPTION OF THE INVENTION

10 The following description provides specific details in order to provide a thorough understanding of the present invention. The skilled artisan would understand, however, that the present invention can be practiced without employing these specific details. Indeed, the present invention can be practiced by modifying the illustrated apparatus and method and can be used in conjunction with apparatus and 15 techniques conventionally used in the industry.

The present invention uses x-ray fluorescence analysis to detect at least one taggant which is intrinsically or extrinsically present in the material of a product or article. With x-ray fluorescence (XRF) analysis, x-rays produced from electron shifts in the inner shell(s) of atoms of the taggants and, therefore, are not affected by the 20 form (chemical bonding) of the article being analyzed. The x-rays emitted from each element bear a specific and unique spectral signature, allowing one to determine whether that specific taggant is present in the product or article.

Figures 1, 2a, and 2b represent how it is believed XRF generally operates. In Figure 1, primary x-rays or gamma rays 40 are irradiated on a sample of a target 25 material 46 of article 42. Secondary x-rays 44 are emitted from that sample of target material 46.

In Figures 2a and 2b, atom 48 of a taggant located within target material 46 has nucleus 50 surrounded by electrons 52 at discrete distances from nucleus 50 (called electron shells). Each electron shell has a binding energy level equal to the 30 amount of energy required to remove that electron from its corresponding shell. The

innermost shell is the K shell, and has the highest binding energy level associated with it. Electron 54 is located within K shell 56.

Primary x-ray or gamma ray photon 40 impacting atom 48 has a given energy. If that energy is greater than the binding energy level of K shell 56, the energy of x-ray photon 40 is absorbed by atom 48, and one of the electrons in K shell 56 (i.e., electron 54) is ejected. With a vacancy now in K shell 56 left by electron 54, atom 48 is energetic and unstable. To become more stable, that vacancy in K shell 56 can be—and usually is—filled by an electron located in a shell with a lower binding energy level, such as L-shell electron 58 in L shell 60. As L-shell electron 58 fills the vacancy in K shell 56, atom 48 emits a secondary x-ray photon 44. The energy levels (or corresponding wavelengths) of such secondary x-ray photons are uniquely characteristic to each taggant, allowing the presence or absence of any specific taggant to be determined.

The at least one taggant can be intrinsically or extrinsically present in the product (or article) to be detected (the “target material”). When the taggant(s) is intrinsically present, it is a component (either as an element, compound, or other type of composition) in at least one portion of that target material. When the taggant(s) is extrinsically present, it can be added, incorporated, or inserted into the target material as described below.

The at least one taggant employed in the present invention can be any suitable taggant known in the art. See, for example, U.S. Patent Nos. 5,474,937, 5,760,394, and 6,025,200, the disclosures of which are incorporated herein by reference. Suitable taggants include any element or compound which is capable of being detected via XRF. The type of elements that can be used as the taggant are theoretically any of those listed in the periodic table, but the lower energy emitted by electrons in the lower atomic-number elements could be a limiting factor. Such lower energies can be re-absorbed much easier into its own material matrix or, in some cases, into the ambient atmosphere (e.g., air). Further, different isotopes of an element, as well as elements which “excite” only under certain conditions—such as specific temperature ranges—could be employed as the taggant in the present invention. Example of

taggants that could be used in the present invention include any element with an atomic number ranging from 6 to 94. Preferably, rare earth metals are used as the at least one taggant in the present invention. More preferably, samarium (Sm) and/or lanthanum (La) are used as the at least one taggant in the present invention.

5        The type of taggant depends, among other things, on the target material in which it is located. The target material can interfere with the XRF detection because, as described below, backscattering and peaks emitted by the composition of the target material during XRF analysis can interfere with the taggant peaks. For example, if paper packaging contained an As taggant and trace amounts of Pb existed in the paper, 10      the K-level electrons of As and L-level electrons of Pb could give confusing readings during XRF detection.

15      In one aspect of the invention, the type of taggant should be selected based on the ability of the taggant and/or the substance in which it is located (i.e., a coating) to attach or bond to the target material. In many instances, the target material will be used, handled, and/or washed extensively. If the taggant (or the substance in which it is located) is removed from the target material under such conditions, tagging the target material is of little value. For example, if a film or coating (e.g., paint) containing a taggant is applied to a target material (e.g., wall), the taggant and coating should be selected so that they will not be removed by the conditions to which the target 20      material is periodically subjected. Preferably, the coating and/or the taggant is selected in this aspect of the invention so that it chemically attaches or bonds to the target material, like paint attaches and bonds with a wall.

25      In another aspect of the invention, the type of taggant should be selected based on the ability of the taggant and/or the substance in which it is located (i.e., a coating) to be removed from the target material. In many instances, the purpose for which the target material is tagged will be temporary. After this purpose is completed, the taggant is no longer needed and can optionally be removed. For example, if an identifying film or coating containing a taggant is applied to a target material, once the target material has been identified, the identifying film or coating may no longer 30      be needed and can be removed by suitable means. Preferably, the coating and/or the

taggant is selected in this aspect of the invention so that it is removable by mechanical or chemical means.

The amount and concentration of the taggant in the target material can also vary depending on the number of elements used and energy needed. The amount of taggant employed in the present invention is determined by the minimum amount needed for XRF detection. Additional amounts of taggant can be used as described below. The concentration of the taggant is at least about 1 part per million (ppm), and can range from about 1-100 ppm. Larger taggant amounts can be used, but for economic reasons, a small amount is sufficient. Even lower taggant concentrations can be used (i.e., less than 1 ppm) as improved XRF devices and techniques become available.

The form of the taggant in the target material can also vary. The form can be any compound (i.e., salt) or molecule—either small or large—containing the element that is added by itself or with other components. Indeed, the taggant can be combined with various components and/or additives to make a mixture and/or solution. These other components or additives can be selected for various purposes, e.g., to modify the XRF properties, to modify the ability to be inserted into an article/product, to stabilize the mixture or solution, or other purpose known in the chemical arts. For example, the taggant could be in the form of a salt of the taggant, such as iodide or chloride.

In one aspect of the invention, the at least one taggant is a combination or plurality of taggants. A plurality of taggants could include more than one taggant of the same type, e.g., the same element or compound. A combination of taggants could also be more than one type of taggant, e.g., a different element or compound in different media. For example, a taggant dispersed in ink which has been placed on paper which also contains the same or different taggant. The plurality of taggants could also include a combination of at least one intrinsic and at least one extrinsic taggant.

The at least one taggant incorporated in the target material can provide a distinctive code. Such a code could be based on the number and types of taggants present or absent, an abundance ratio (i.e., concentrations) of the same or different

taggants, the location of the taggants within the material (i.e., a barcode made of a series of taggants with a space, where the space could be part of the code), the presence of multiple types or forms of a single taggant, or a combination thereof.

As one example of such a code, the present invention can include a system in 5 which the concentration of one taggant in a targeted material is controlled to provide a distinctive code. For example, for tagging ten commercially prepared batches of a product, a specific taggant can be used. Ten unique codes could then be created for these ten batches by preparing samples of the target material containing various concentrations (i.e., 10 ppm, 20 ppm, ... 100 ppm) of that taggant.

10 The number of unique codes available with the use of just a single taggant depends on the precision with which that concentration can be controlled and measured in the sample. For example, if techniques allow concentrations in about 10 ppm increments, 10 unique codes (i.e., 10 ppm, 20 ppm, ... 100 ppm) can readily be constructed from a single taggant for that concentration range. Additional codes 15 could be created for larger concentration ranges, e.g., 100 codes of a concentration ranging from 10 ppm to 1000 ppm in 10 ppm increments. With the advent of superior concentration and detection techniques (e.g., for smaller increments), more codes may be constructed.

Further, the number of unique codes can be increased by adding additional 20 types and concentrations of the same or different taggants. A significant increase in the number of possible codes can be achieved by using more than one taggant in creating the code. For example, the code can be expanded by adding another taggant with its own specific concentrations. The number of codes can be further expanded by adding a third taggant with its own specific concentrations. Additional taggants 25 could be used to provide even more codes. This coding system depends on the concentration increments of each of the taggants.

The number of codes available in the coding system could also be increased by varying the location of the taggant(s) within the material to be detected. For example, the detected material could be divided into any number of portions (i.e., quadrants)

with certain taggants (or codes) being placed in certain of those portions, and optionally not in others, to signify additional information during the XRF analysis.

When taggants include elements or compounds that may be found in the target material or in the environment to which the target material may be exposed, taggant contamination may occur and possibly render the taggant code difficult to read. For example, if the taggant comprising lanthanum is located in a target material, it is possible that additional amounts of the taggant(s) could be present in the target material as a result of environmental contamination, an internal chemical reaction, or other contamination. If this contamination occurs, there will be a change in the concentration of that taggant in the target material. Subsequent measurement of this taggant could yield a value corresponding to an incorrect code.

In such an instance, it is difficult to determine what amount of the taggant present in the targeted material is "contamination" as opposed to taggant present before contamination. This problem can be solved in target materials for which contamination might be suspected by using a backup (i.e., duplicate or otherwise) or secondary system, such as a backup or secondary taggant(s), backup or secondary code, or backup or secondary location. See, for example, the description in U.S. Patent No. 5,760,394, the disclosure of which is incorporated herein by reference. If desired, more than one such backup or secondary system can be used. The backup or secondary system can also be used for other purposes, e.g., to verify the original coding system.

Any suitable target material can be employed in the present invention. Suitable target materials include those which intrinsically contain the desired taggant(s) or in which the desired taggant(s) can be incorporated. Because XRF detection measures changes in the inner shell(s) of the taggant, it will not be significantly modified by chemical reactions that normally occur in the outer shells. Thus, it is possible to tag chemicals and have the taggant code be carried in any product manufactured with those chemicals. Target materials should be comprised of a material in which XRF detection is easy, e.g., little chance of background

contamination, taggant deterioration, taggant destruction, contamination, or other deteriorating condition.

Examples of suitable target materials include: paper products like documents, currency, or tickets; solid products like jewelry, carpets, packaging (films, labels, and adhesives), metals, rubbers (tires), woods, or plastics (credit cards); liquid products like lubricating fluids, resins, sprays, paints, oils, inks; hazardous wastes; drugs or pharmaceuticals; gaseous products; or combinations or hybrids of these materials. Additionally, suitable target materials—such as paper documents, drugs, or counterfeit manufactured items—include those that will be subsequently changed. For example, a target material that is suspected might be destroyed could be tagged with elements known to be present in the residue from the destruction. Since the taggant is not usually changed by the chemical process in destruction, a connection between the target material and its residue could be established after destruction. Preferably, the target material of the present invention is paper and paper-based products. Examples of paper and paper products include tickets and coupons.

The target materials containing the at least one taggant can be used for a wide number of applications. For example, tagging paints would allow any article coated with that paint to be identified. In another example, tagging paper and ink used in the paper (or applied to the paper) can be used to establish the authenticity of documents and currency. In yet another example, many manufactured items prone to counterfeiting or theft could benefit from tagging. Tagged threads in clothing could be used to encode information about the date, time, and place of manufacture. Tagging the bulk materials used in the manufacture of such items as compact disks, computer disks, video tapes, audio tapes, electronic circuits, and other items would be useful in tracing and prosecuting theft and counterfeiting cases involving these items. Tagging the packaging placed on products would allow quick and easy tracking of the packaged products.

In the present invention, the at least one taggant can be incorporated into the target material in any suitable form. Suitable forms include those which place that taggant in the target material with little to no damage (either chemical or physical) to

the target material. See, for example, the description in U.S. Patent Nos. 5,208,630, 5,760,394, and 6,030,657, the disclosures of which are incorporated herein by reference. Other suitable forms include using materials containing the taggant such as particulates like microparticles; solvents; coatings and films; adhesives; sprays; or a 5 hybrid or combination of these methods. In any of these forms, the at least one taggant can be incorporated by itself or with another agent.

The at least one taggant can be incorporated in the target material using any suitable technique. Many existing tagging techniques involve the use of microparticles containing the elements, or compounds or compositions of the 10 elements, comprising the at least one taggant. Additionally, particles can be manufactured wherein smaller particles, or compounds or compositions of the elements, containing the taggant. Such particles could be made of: magnetic or fluorescent materials to facilitate collection; refractory materials to enhance particle survival in an explosion; or chemically inert materials to enhance particle survival in a 15 chemical reaction. Indeed, such particles could be made of non-durable, soluble, or reactive materials to enhance taggant dispersal in a fluid, aerosol, or powder system.

When the target material is a liquid article like paints, inks, or adhesives, or has a liquid component, the at least one taggant can be incorporated as an element or compound in solution with the liquid. Thus, the at least one taggant can be 20 incorporated in elemental or compound form either in solution or suspension in the target material. The at least one taggant could also be dissolved or suspended in a solvent used in making the target material so that when that solvent evaporates, the residue left behind would contain the at least one taggant.

The taggant can be inserted into the target material of an article either during 25 or after the article (or a part thereof) has been manufactured. The taggant can be manufactured as a component of the article or as part of a component of the article. During manufacture, the at least one taggant can also be incorporated into another material which comprises part of the article. Indeed, the at least one taggant could also be an element or compound of the article itself. The taggant can be incorporated 30 into any location (including surfaces) of the article. Two (and three) dimensional

shapes and patterns of the at least one taggant can be constructed using any desired combination of types and numbers of taggants.

The at least one taggant could also be incorporated after manufacture of the target material of the article. The taggant can be implanted into the article or 5 deposited as a coating or film on the article. Additionally, the at least one taggant could be incorporated into the already formed article as a dopant.

As a coating or film, the at least one taggant could be physically or chemically deposited by itself. The at least one taggant could also be incorporated as one 10 ingredient (or contaminant) of another material (such as a mixture or solution) which forms a coating or film. In this aspect of the invention, the at least one taggant can be incorporated as an element or compound in solution (or suspension) with a liquid which is applied, such as by spraying or dipping, to the article. For example, the at 15 least one taggant could be dissolved or suspended in a solvent so that when that solvent evaporates after being applied to the article, the residue left behind would contain the at least one taggant.

As apparent from the description above, the present invention has the ability to easily tag small batches of target materials with a code unique to that batch. This can be done manually or in an automated system where each batch (or select batches) of the target material receives a different code. For example, 1000 (or 100) compact 20 discs could be manufacture and each could be tagged with a code of a number from 1 to 1000 (or 1 to 100). Economic and processing considerations, however, might limit the minimum size of each batch and the number of batches which could be tagged.

As described above, any product or article as the target material can have at least one extrinsic or intrinsic taggant located therein. In one aspect of the present 25 invention, the target material of the present invention could be a commercially-available product which can be modified with the processes described herein. For example, the target material could be paper tickets which are purchased and then at least one taggant is incorporated in or on the tickets. In another aspect of the invention, the target material of the present invention can be made with the processes 30 described herein. For example, the target material could be paper tickets which are

manufactured with the at least one taggant already incorporated in or on such tickets. In another aspect of the invention, the at least one taggant could also be incorporated into the paper or ink of a ticket by any suitable implantation or diffusion method.

5 The at least one taggant could be incorporated into the components of the paper from which the tickets are made. Paper is made from cellulose as well as other components. These components are used in well known processes to make paper sheets or rolls. Thus, the at least one taggant could be added to the cellulose (or the other components) before or during this conversion process so that the paper rolls or sheets have the at least one taggant incorporated therein.

10 The at least one taggant could also be incorporated into the paper before the tickets are made. For example, the at least one taggant could be added during the sizing process. Sizing is a well-known process by which the paper surface is made resistant to moisture and abrasion while improving the finish, printability, smoothness and surface bonding strength. This is accomplished by spraying a sizing liquid on the 15 paper sheet, compressing it, and drying it. As the sizing liquid penetrates the fibers of the paper, the components of the sizing liquid (i.e., starch) interweaves with the fibers in a permanent bond. Adding the taggant to the sizing liquid could ensure that the taggant permanently bonds to the paper. In another example, after the paper sheet has been made, it is cut to the desired size. The at least one taggant could also be added 20 during this cutting operation.

25 The at least one taggant could be incorporated into the ink or other writing on the tickets. After the paper sheet or tickets are made, the ink (or other writing) is respectively deposited on the paper sheet(s) or tickets. The at least one taggant could be incorporated into the ink (or other writing) before, during, or after the process of its deposition.

30 The at least one taggant could also be incorporated into a film or coating which is placed on the tickets. Often, a coating or film is placed on the tickets for many reasons. In this aspect of the invention, the at least one taggant can be first dispersed in a solution containing a suitable solvent. This solution is then placed on the ticket(s) and allowed to dry, with the solution (including solvent) partially or fully

evaporating and leaving the at least one taggant as a component of the coating or film. The solution can be placed on the tickets using any suitable chemical deposition method, such as by spraying or by dipping.

The at least one taggant could be incorporated into tickets with each ticket (or 5 group of tickets) having its own code. As one example, tickets for different events or geographical locations could have a different taggant mix incorporated therein. Assuming two taggants will be used, a number of automated reservoirs having varying concentrations of the two taggants could be included in the sizing stage of the paper making process. Each reservoir would contain a distinctive mix of taggant 10 concentrations, e.g., 5/5, 5/10, 5/15,...10/5, 10/10, 10/15, ... 95/85, 95/90, 95/95. As any particular paper sheet passes through the assembly line, it would receive the taggants from the desired reservoir. Thus, each paper sheet and the tickets cut from that sheet could receive a unique combination of taggants for its code.

After the at least one taggant is extrinsically or intrinsically present in the 15 target material(s), the taggant(s) is detected to identify or verify the target material using XRF analysis as illustrated in Figure 1. Primary x-rays 40 are used to excite a sample of the target material 46, and the secondary x-rays 44 that are emitted by the sample are detected and analyzed.

As shown in Figure 3, the x-rays which are detected have various energies, 20 e.g., there is a broad band of scattered x-rays with energies less than and greater than those of the exciting atom. Figure 3 illustrates this spectrum for paper as the target material. Within this broad band, there are peaks due to the excitation of the taggant(s) in the sample. The ratio of the intensity of the radiation in any peak to the intensity of the background at the same energy (known as the peak-to-background ratio) is a 25 measure of the concentration of the element which has characteristic X-rays at the energy of that peak, e.g., the taggant.

In one aspect of the detection method of the present invention, at least one target material believing to contain known concentrations of the taggant(s) of interest is selected. The XRF analysis is performed on that target material (or a sample 30 thereof) using a detection device or apparatus containing an x-ray radiation source

("source"), x-ray radiation detector ("detector"), support means, analyzer means, and calibration means.

One aspect of the detection device of the present invention is illustrated in Figure 4a. In this Figure, the detection apparatus 25 has an ordinary x-ray fluorescence spectrometer capable of detecting elements present in a coating or packaging material. X-rays 29 from a source (e.g., either x-ray tube or radioactive isotope) 20 impinge on a sample 11 which absorbs the radiation and emits x-rays 31 to an x-ray detector 21 and analyzer 23 capable of energy or wavelength discrimination. This is accomplished by using a commercially available x-ray spectrometer such as an Edax DX-95 or a MAP-4 portable analyzer, commercially available from Edax Inc., Mahwah, New Jersey. Part of analyzer 23 includes a computerized system 27.

Another aspect of the detection apparatus of the present invention is illustrated in Figure 4b. In this Figure, the detection apparatus 25 has an instrument housing 15 which contains the various components. Gamma rays or x-rays 30 from a source (e.g., either x-ray tube or radioactive isotope) 20 are optionally focused by aperture 10 to impinge on a sample 11. Sample 11 contains the at least one taggant which absorbs the radiation and emits x-rays 31 to an x-ray detector 21. Optionally, analyzing means can be incorporated within housing 15.

The present invention, however, is not limited to the detection apparatus depicted in Figures 4a and 4b. Any suitable source, or plurality of sources, known in the art can be used as the source in the detection device of the present. See, for example, U.S. Patent Nos. 4,862,143, 4,045,676, and 6,005,915, the disclosures of which are incorporated herein by reference. During the XRF detection process, the source bombards the taggant with a high energy beam. The beam may be an electron beam or electromagnetic radiation such as X-rays or gamma rays. The source, therefore, may be any material which emits such high energy beams. Typically, these have been x-ray emitting devices such as x-ray tubes or radioactive sources.

To target, the beam can be focused and directed properly by any suitable means such as an orifice or an aperture. The configuration (size, length, diameter...)

of the beam should be controlled, as known in the art, to obtain the desired XRF detection. The power (or energy level) of the source should also be controlled, as known in the art, to obtain the desired XRF detection.

The source(s) can be shielded and emit radiation in a space limited by the 5 shape of the shield. Thus, the presence, configuration, and the material used for shielding the source should be controlled for consistent XRF detection. Any suitable material and configuration for that shield known in the art can be employed in the present invention. Preferably, any high-density materials used as the material for the shield, e.g, tungsten or brass.

10 Any suitable detector, or plurality of detectors, known in the art can be used as the detector in the detection device of the present invention. See, for example, U.S. Patent Nos. 4,862,143, 4,045,676, and 6,005,915, the disclosures of which are incorporated herein by reference. Any type of material capable of detecting the photons omitted by the taggant may be used. Silicon and CZT (cadmium-zinc-telluride) detectors have been conventionally used, but others such as proportional 15 counters, germanium detectors, or mercuric iodide crystals can be used.

Several aspects of the detector should be controlled to obtain the desired XRF detection. First, the geometry between the detector and the target material should be controlled. The XRF detection also depend on the presence, configuration, and 20 material—such as tungsten and beryllium—used as a window to allow x-rays photons to strike the detector. The age of the detector, voltage, humidity, variations in exposure, and temperature can also impact the XRF detection and, therefore, these conditions should be controlled.

The analyzer means sorts the radiation detected by the detector into one or 25 more energy bands and measures its intensity. Thus, any analyzer means performing this function could be used in the present invention. The analyzer means can be a multi-channel analyzer for measurements of the detected radiation in the characteristic band and any other bands necessary to compute the value of the characteristic radiation as distinct from the scattered or background radiation. See, for example, 30 U.S. Patent Nos. 4,862,143, 4,045,676, and 6,005,915, the disclosures of which are

incorporated herein by reference.

The XRF also depends on the resolution of the x-rays. Background and other noise must be filtered from the x-rays for proper measurement, e.g., the signals must be separated into the proper number of channels and excess noise removed. The 5 resolution can be improved by cooling the detector using a thermoelectric cooler—such as a nitrogen or a peltier cooler—and/or by filtering. Another way to improve this resolution is to use pre-amplifiers.

The support means supports the source and detector in predetermined positions relatively to a sample of the target material to be irradiated. Thus, any support means 10 performing this function could be used in the present invention. In one example, the support means comprises two housings, where the source and detector are mounted in a first housing which is connected by a flexible cable to a second housing in which the analyzer means is positioned as illustrated in Figure 4a. If desired, the first housing may then be adapted to be hand-held. In another example, the source and detector as 15 well as the other components of the detection device are mounted in a single housing as illustrated in Figure 4b.

The calibration means are used to calibrate the detection apparatus, thus insuring accuracy of the XRF analysis. In this calibration, the various parameters which could be modified and effect the measurement are isolated and calibrated. For 20 example, the geometrical conditions or arrangements can be isolated and calibrated. In another example, the material matrix are isolated and calibrated. Preferably, internal (*in situ*) calibration during detection is employed as the calibration means in the present invention. Components, such as tungsten shielding, are already present to internally calibrate during the XRF analysis. Other methods, such as fluorescence 25 peak or Compton backscattering, could be used for internal calibration in the present invention.

Analyzer means, which includes a computerized system 27, is coupled to, receives, and processes the output signals produced by detector 21. The energy range of interest, which includes the energy levels of the secondary x-ray photons 44 30 emitted by the taggant(s), is divided into several energy subranges. Computerized

system 27 maintains counts of the number of X-ray photons detected within each subrange using specific software programs, such as those to analyze the detection and x-ray interaction and to analyze backscatter data. After the desired exposure time, computerized system 27 with display menus stops receiving and processing output signals and produces a graph of the counts associated with each subrange.

Figure 5 is a representative graph of the counts associated with each subrange. This graph is essentially a histogram representing the frequency distribution of the energy levels E1, E2, and E3 of the detected x-ray photons. Peaks in the frequency distribution (i.e., relatively high numbers of counts) occur at energy levels of scattered primary x-ray photons as well as the secondary x-ray photons from the taggant(s). A primary x-ray photon incident upon a target material may be absorbed or scattered. The desired secondary x-ray photons are emitted only when the primary x-ray photons are absorbed. The scattered primary x-ray photons which reach the detector of the system create an unwanted background intensity level. Accordingly, the sensitivity of XRF analysis is dependent on the background intensity level, and the sensitivity of XRF detection may be improved by reducing the amount of scattered primary x-ray photons reaching the detector. The peak occurring at energy levels of scattered primary x-ray photons is basically ignored, while the other peaks—those occurring at E1, E2, and E3—are used to identify the at least one taggant present in the target material.

Besides the parameters described above, at least two other parameters must be controlled during the process of XRF detection. First, the media (such as air) through which the gamma rays (and x-rays) must travel also impacts the XRF. Therefore, the different types of media must be considered when performing the XRF analysis. Second, the methods used to interpret and analyze the x-rays depend, in large part, on the algorithms and software used. Thus, methods must be adopted to employ software and algorithms that will consistently perform the XRF detection.

These two parameters, plus those described above, must be carefully accounted for and controlled to obtain accurate measurements. In one aspect of the intention, these parameters could be varied and controlled to another provide a distinct

code. For example, using a specific source and a specific detector with a specific measuring geometry and a specific algorithm could provide one distinct code. Changing the source, detector, geometry, or algorithm could provide a whole new set of distinct codes.

5 Figure 6 illustrates a preferred apparatus and detection method according to the present invention. In this Figure, detection apparatus 25 is capable of detecting at least one taggant present in target material 10, such as a ticket. Detection apparatus 25 is a portable device which can be small enough to be hand-held. Detection apparatus 25 contains all the components discussed above (i.e., source, detector, 10 analyzer means, and calibration means) in a single housing, thus allowing the portability and smaller size.

The present invention is not limited to any specific XRF analysis. Any type of XRF, such as total reflection x-ray fluorescence (TXRF), can be employed in the present invention.

15 In one aspect of the invention, the apparatus and method used identify an article once it has been tagged. The ability to invisibly tag an article and read the tag, especially with a non line-of-sight method, would provide an invaluable asset in any industry that authenticates, verifies, tracks, labels, or distributes goods of any kind. Indeed, having an invisible taggant(s) could further prevent copying and 20 counterfeiting of goods. In another aspect of the invention, the apparatus and method of the present invention could be used for these same purposes, but for those products that have the desired taggant already located therein. Thus, the present inventions could analyze liquid flows for contaminant particles or pinpoint via 3-D analysis the exact location of a contaminant(s) in an article.

25 The following non-limiting examples illustrate the present invention.

Example 1

A dispersion of lanthanum oxide (taggant) particles in water was added to a sizing bath at a paper-manufacturing mill to obtain a taggant concentration in the bath of 7500 ppm lanthanum. The paper to be tagged, referred to as the "web," was then 30 run through the bath as part of the manufacturing process and soaked up the tagged

solution. The web was then heat dried to drive off the water through evaporation, leaving the "size" and taggant as integral parts of the paper fiber.

Example 2

A specialty ink base was prepared by adding a phosphomolybdc acid complex 5 pigment to water which also contained resin and de-foaming agents. The concentration of the taggant in the base was 35 wt% molybdenum (taggant). Two liters of this base was sent to a ticket printer to make a black printing ink for tickets. The printer applied the black printing ink to card stock tickets using a flexographic printing press. The ink was allowed to dry on the card stock tickets, leaving the 10 taggant as part of the dried ink.

Example 3

The tagged ticket from Example 2 was analyzed for the presence of the molybdenum taggant. A portable, hand-held detection apparatus similar to that 15 illustrated in Figure 6 was used to detect the presence of the taggant using XRF analysis.

The detection apparatus contained several components. A trigger actuated tungsten shutter block containing an americium 241 gamma ray point source and a silicon pin x-ray detector were located within the front of the instrument. Circuit boards, necessary for acquiring and processing the data from the detector were located 20 within the rest of the housing. The instrument had a red and a green light to indicate whether the carpet was tagged or not and a read out to inform the user that the carpet was tagged or not. A keypad on the top of the instrument allowed the user to turn the electronics of the instrument on and off, while a key operated lock on the side of the instrument kept the user from inadvertently opening the shutter block, exposing the 25 radioactive source.

This detection apparatus was used for an XRF analysis on the tagged ticket. The result of the XRF analysis for the tagged ticket is reported in Figure 7. The peaks indicating the presence of the molybdenum taggant in Figure 7 are labeled.

Having described the preferred aspects of the present invention, it is 30 understood that the invention defined by the appended claims is not to be limited by

particular details set forth in the above description, as many apparent variations thereof are possible without departing from the spirit or scope thereof.

CLAIMSWe claim:

1. A method for detecting at least one taggant on an article, comprising:  
providing at least one taggant on at least a portion of an article;  
causing the at least one taggant to radiate at least one x-ray; and  
analyzing whether the at least one x-ray has a specific energy.  
5
2. The method of claim 1, wherein the article is at least one ticket.
3. A method of analyzing an article, comprising  
providing a portion of the article;  
10 irradiating that portion with an energy beam; and  
analyzing whether that portion irradiates at least one x-ray with a specific  
energy.
4. The method of claim 3, wherein the at least one article is at least one  
ticket.
- 15 5. A method for coating an article with at least taggant, comprising:  
providing a portion of an article; and  
providing a coating on the portion of the article, the coating comprising at  
least one taggant which radiates at least one x-ray when an energy beam is impinged  
thereon.
- 20 6. The method of claim 5, wherein the at least one article is at least one  
ticket.
7. A coating for at least one article, the coating comprising at least one  
taggant which radiates at least one x-ray when an energy beam is impinged thereon.
- 25 8. The coating of claim 7, wherein the at least one article is at least one  
ticket.
9. A taggant solution, comprising:  
at least one taggant, the at least one taggant radiating at least one x-ray when  
an energy beam is impinged thereon; and  
at least one solvent, at least a portion of the solvent evaporating when the  
30 taggant solution is provided on at least one article.

10. The taggant solution of claim 9, wherein the at least one article is at least one ticket.

11. A method of manufacturing at least one article containing at least one taggant, comprising:

5 providing a portion of the article; and

providing a coating on the portion of the article, the coating comprising at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon.

12. The method of claim 11, wherein the at least one article is at least one ticket.

13. An article containing at least one taggant made by the method comprising:

providing a portion of the article; and

15 providing a coating on the portion of the article, the coating comprising at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon.

14. The article of claim 13, wherein the article is at least one ticket.

15. An article comprising a coating containing at least one taggant, the at least one taggant radiating at least one x-ray when an energy beam is impinged 20 thereon.

16. The article of claim 15, wherein the at least one article is at least one ticket.

17. A method of tagging an article with at least one taggant comprising:

providing a portion of the article; and

25 providing a coating containing at least one taggant on that portion of the article, the at least one taggant radiating at least one x-ray when an energy beam is impinged thereon.

18. The method of claim 17, wherein the article is at least one ticket.

19. A method for detecting at least one taggant in an article, comprising:

30 providing at least one taggant in a portion of an article;

causing the at least one taggant to radiate at least one x-ray; and  
analyzing whether the at least one x-ray has a specific energy.

20. The method of claim 19, wherein the article is at least one ticket.

21. A method of tagging an article with at least one taggant comprising:  
5 providing a portion of an article; and  
providing at least one taggant in a portion of the article, the at least one taggant  
radiating at least one x-ray when an energy beam is impinged thereon.

22. The method of claim 21, wherein the article is at least one ticket.

23. A method for making at least one ticket containing at least one taggant,  
10 comprising:  
providing a sheet comprising the at least one taggant which radiates at least  
one x-ray when an energy beam is impinged thereon;

providing ink on the sheet; and  
cutting the sheet into at least one ticket.

15. A method for making at least one ticket containing at least one taggant,  
comprising:  
providing a sheet;

providing ink on the sheet, the ink comprising the at least one taggant which  
radiates at least one x-ray when an energy beam is impinged thereon; and

20. cutting the sheet into at least one ticket.

25. A method for making at least one ticket containing at least one taggant,  
comprising:  
providing a sheet;

providing ink on the sheet; and  
25 cutting the sheet into at least one ticket while incorporating at least one taggant  
into the at least one ticket, the at least one taggant radiating at least one x-ray when an  
energy beam is impinged thereon.

26. A method for making a ticket containing at least one taggant, comprising:  
providing a ticket;

implanting or diffusing at least one taggant into the ticket, the at least one taggant radiating at least one x-ray when an energy beam is impinged thereon.

27. At least one ticket containing at least one taggant made by the method comprising:

5 providing a sheet comprising the at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon;  
providing ink on the sheet; and  
cutting the sheet into at least one ticket.

28. At least one ticket containing at least one taggant made by the method  
10 comprising:

providing a sheet;  
providing ink on the sheet, the ink comprising the at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon; and  
cutting the sheet into at least one ticket.

15 29. At least one ticket containing at least one taggant made by the method comprising:

providing a sheet;  
providing ink on the sheet; and  
cutting the sheet into at least one ticket while incorporating at least one taggant  
20 into the at least one ticket, the at least one taggant radiating at least one x-ray when an energy beam is impinged thereon.

30. At least one ticket containing at least one taggant made by the method comprising:

providing a ticket;  
25 implanting or diffusing at least one taggant into the ticket, the at least one taggant radiating at least one x-ray when an energy beam is impinged thereon.

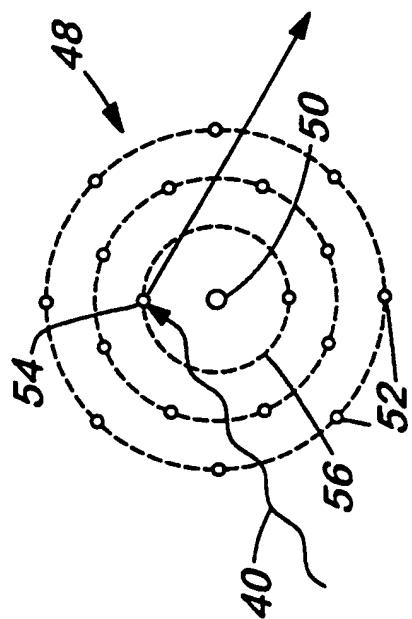
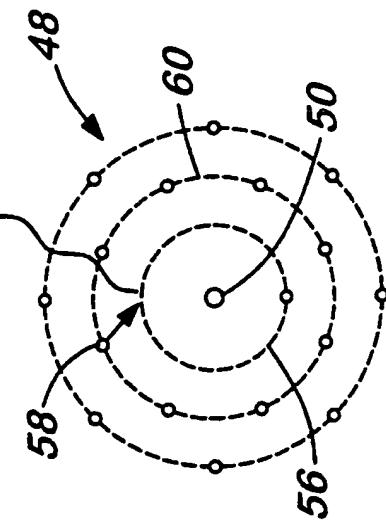
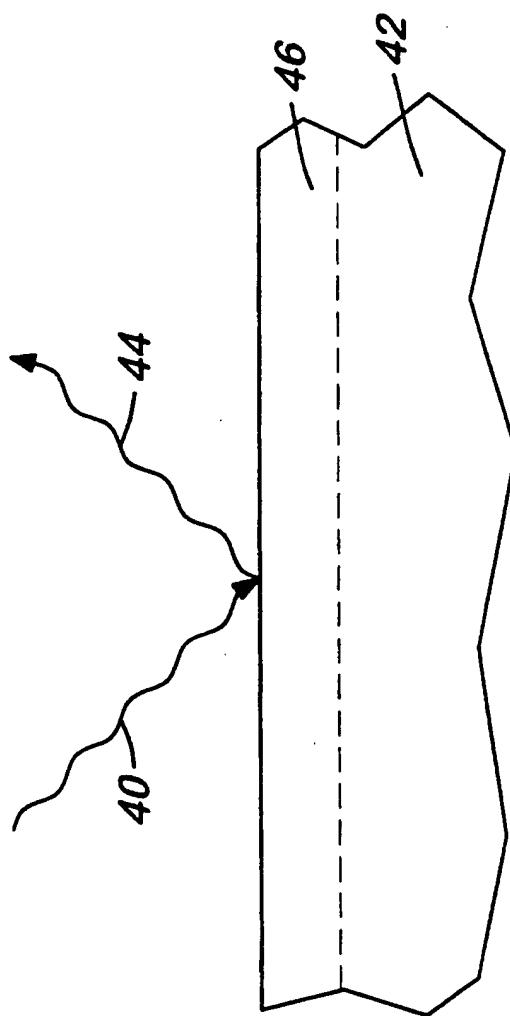
31. A ticket comprising at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon.

32. A ticket comprising:

at least one fiber containing at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon; and  
an ink.

33. A ticket comprising:  
5 at least one fiber; and  
an ink containing at least one taggant which radiates at least one x-ray when an energy beam is impinged thereon.

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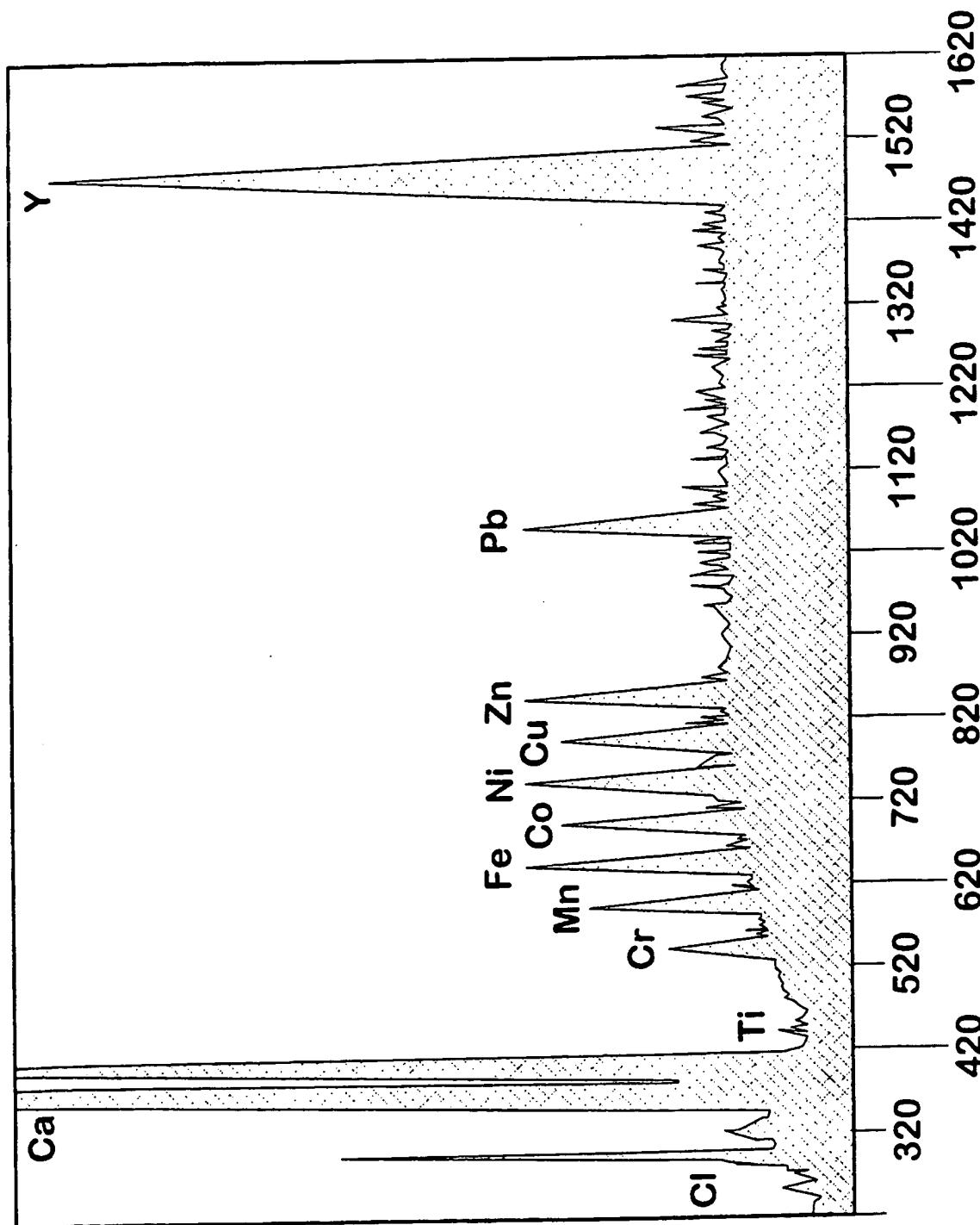
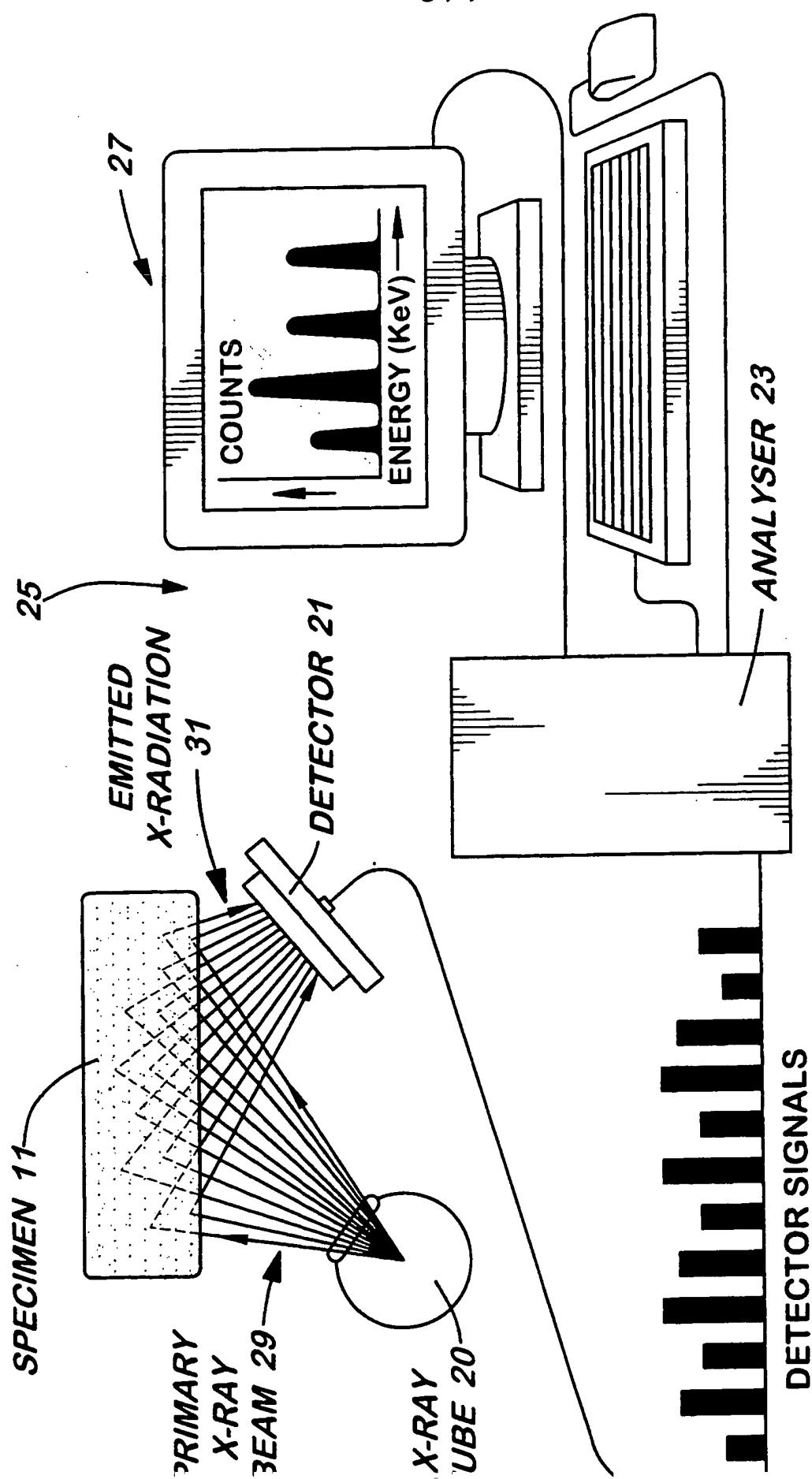


FIG. 3

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FIG. 4a

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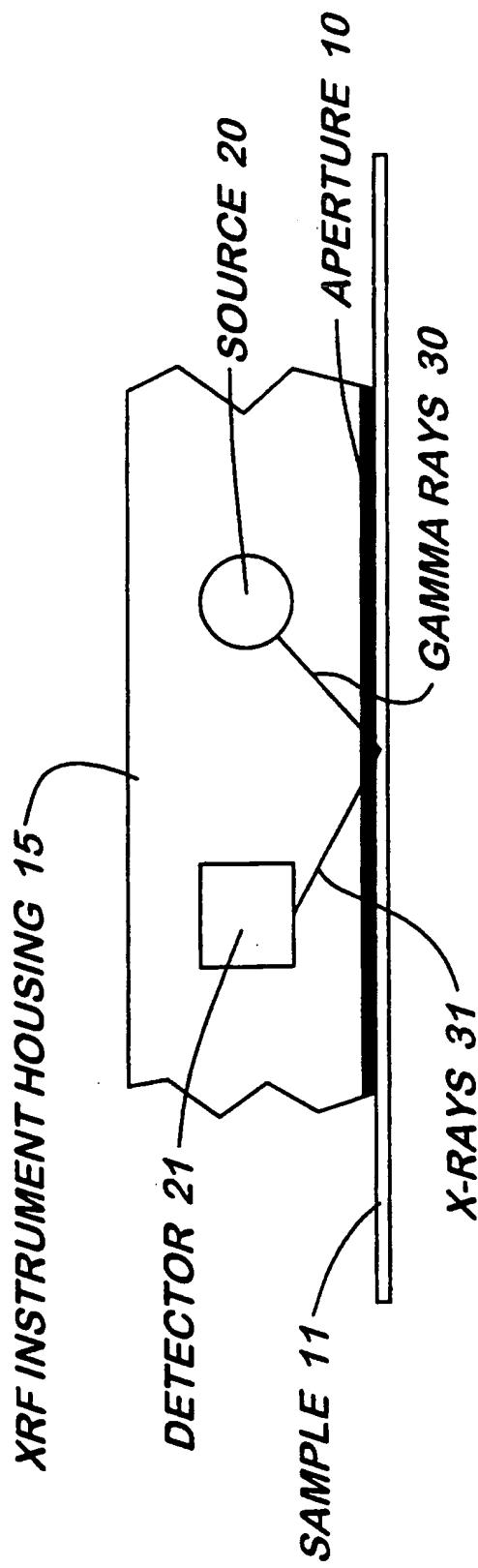
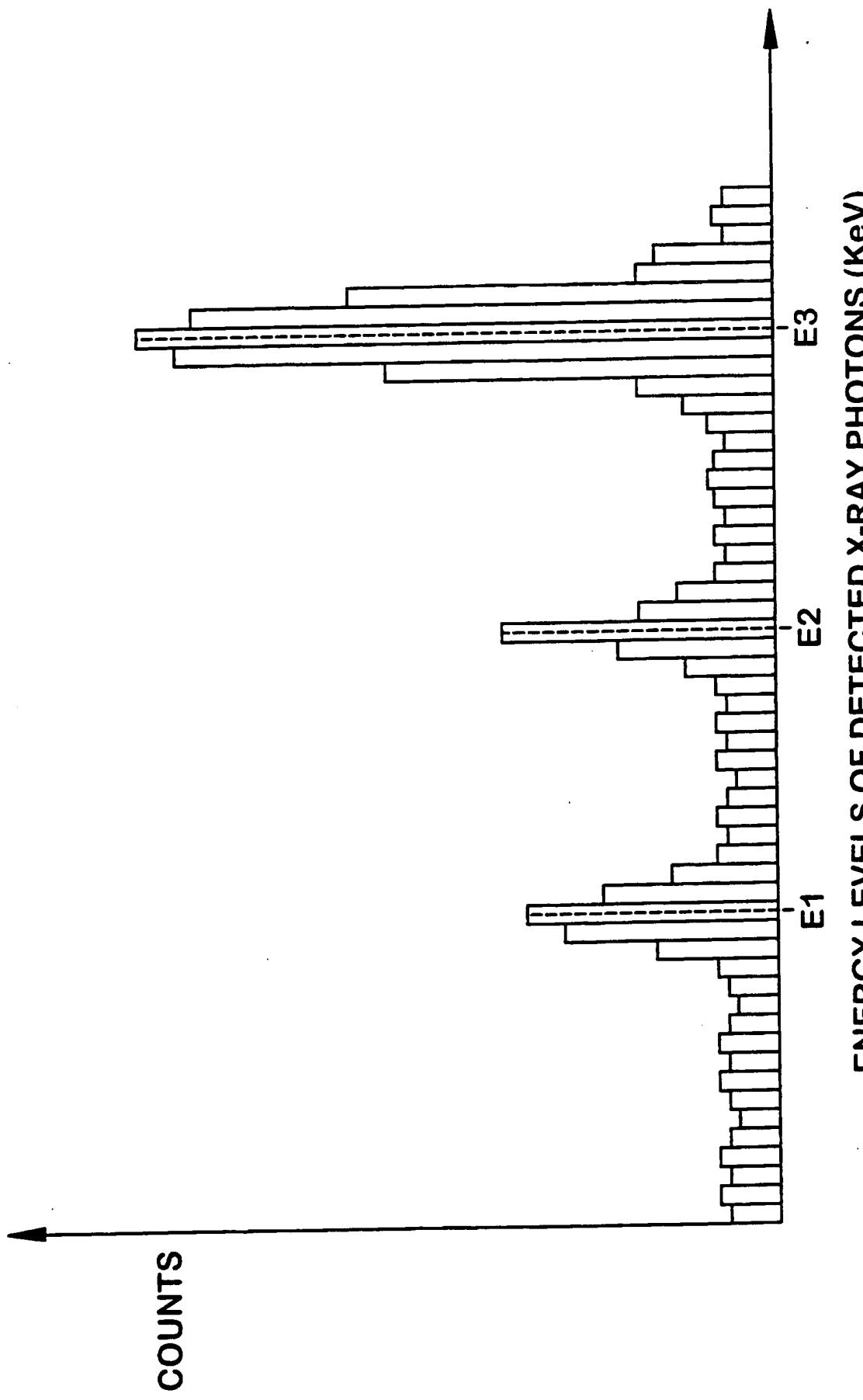


FIG. 4b

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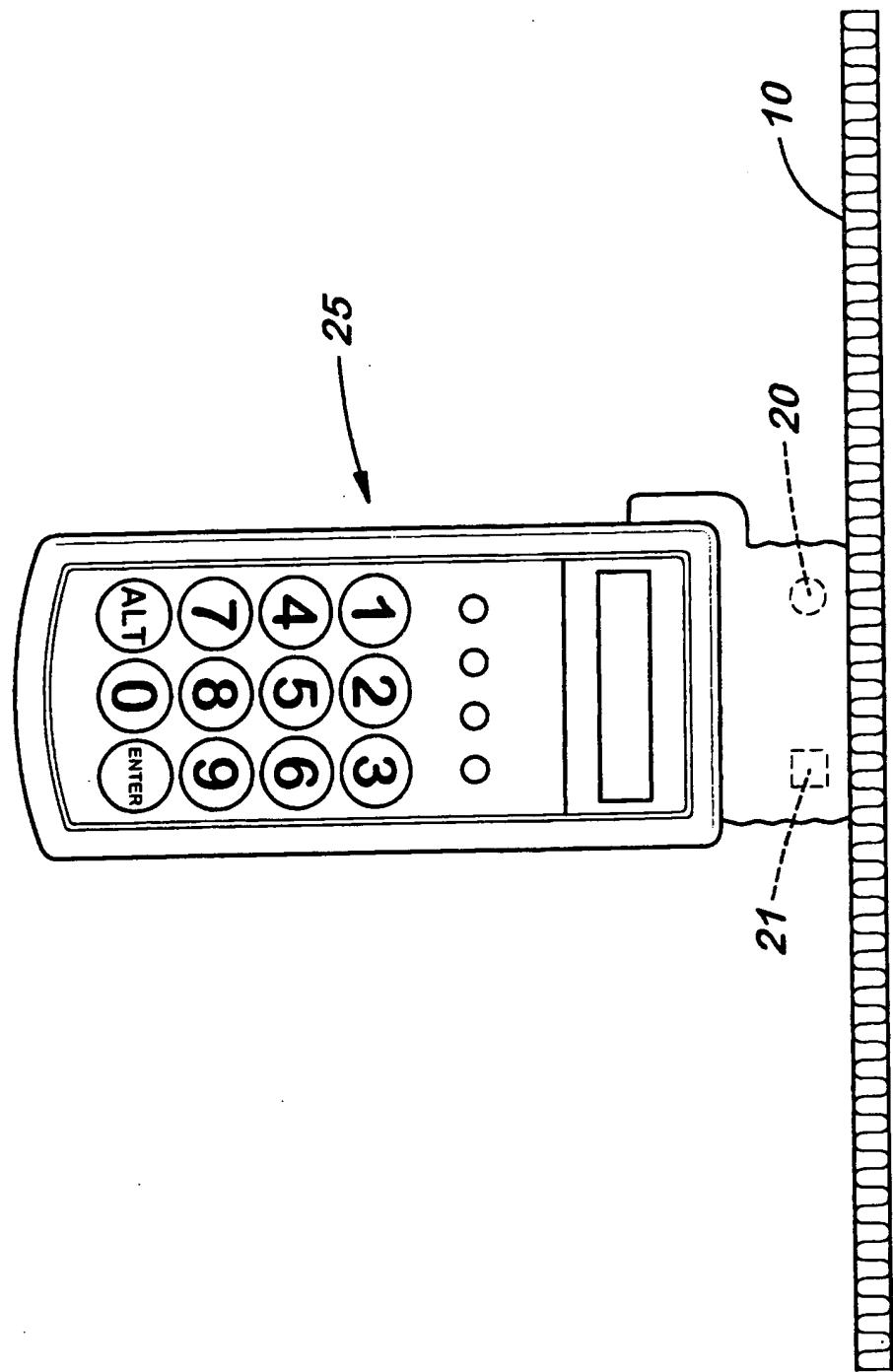


FIG. 6

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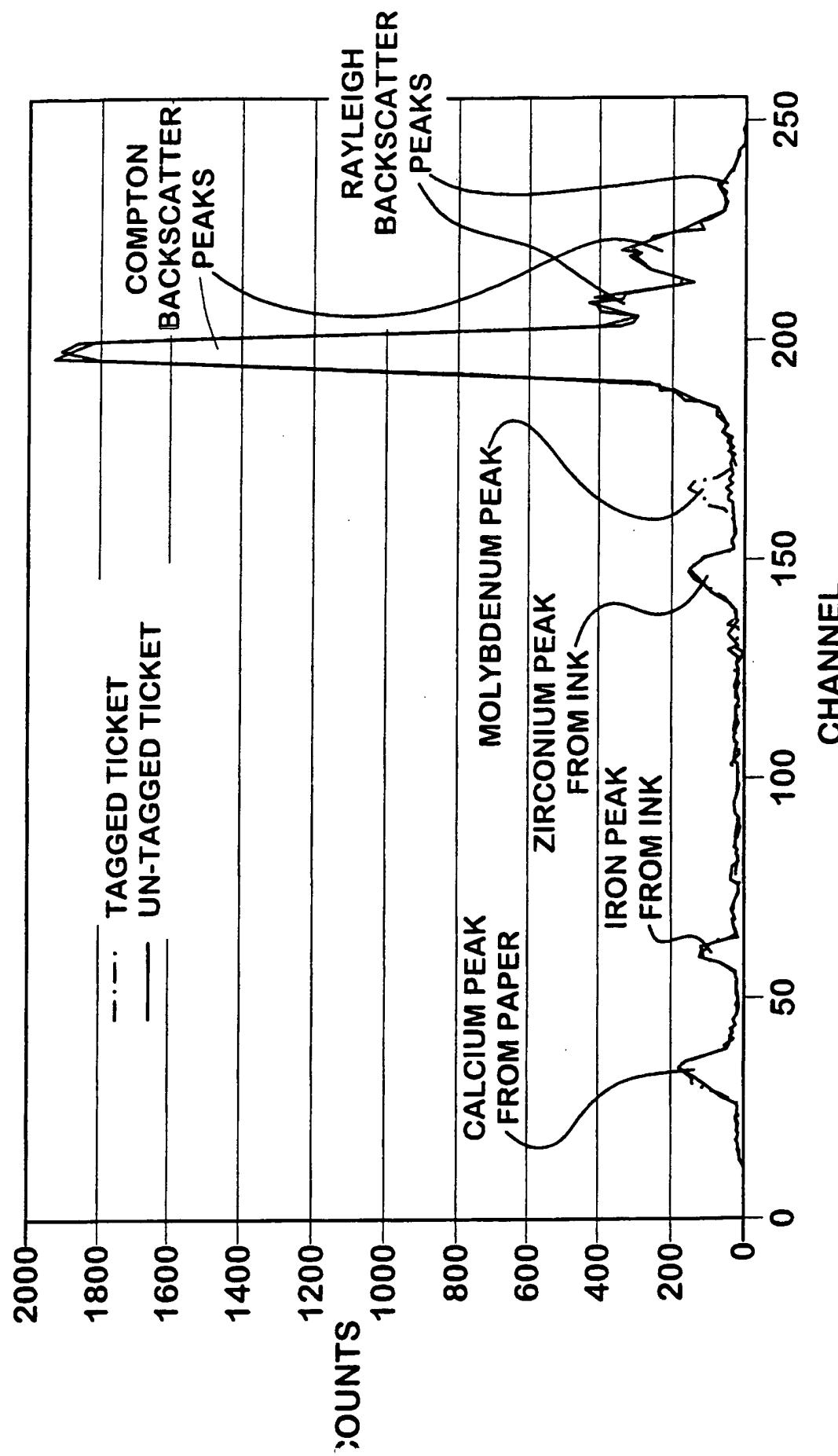


FIG. 7

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/27491

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 23/223  
US CL : 378/44, 45

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 378/44, 45, 48, 49, 50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,445,225 A (WHITE) 24 April 1984 (24.04.1984), column 8, lines 20-62.	1-33
Y	US 4,136,778 A (WORTMAN et al.) 30 January 1979 (30.01.1979), column 4, lines 10-30.	1-33
Y	US 4,485,308 A (RABATIN) 27 November 1984 (27.11.1984), column 3, lines 23-53.	1-33

Further documents are listed in the continuation of Box C.

See patent family annex.

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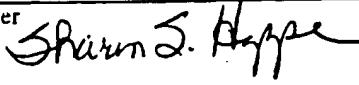
Date of the actual completion of the international search

25 January 2001 (25.01.2001)

Date of mailing of the international search report

16 FEB 2001

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